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VAPOUR-PHASE MODIFICATION OF SORBENTS IN GAS-LIQUID CHROMATOGRAPHY

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SUMMARY

Some theoretical and practical aspects of chromatography with vapour mobile phases are recognized in the course of controlled modification of a stationary liquid phase by vapour eluents. It is shown that the stationary liquid phase is modified temporarily and acquires a different polarity. In consequence, the character of the adsorbate-adsorbent interaction is changed.

INTRODUCTION

At present hundreds of different substances are used as stationary liquid phases in gas-liquid chromatography (GLC). The choice of the optimal stationary liquid phase for solving a specific problem requires great experience and therefore it is imperative to know the general characteristics of the sorbate and stationary liquid. In practice, the characterization of the sorbate class and adsorbent polarity is used as a first approximation for solving such problems. Most substances can be separated by controlling the polarity of the stationary liquid. To this end mixed liquid phases are composed of phases of different polarities in desired ratios. Another method for polarity control consists in the application of multisectional columns containing phases of different polarities. However, such approaches to polarity control are laborious (such polarity control is discrete). In our view, the variation of the adsorptive properties of sorbents by application of vapour mobile phases of different characteristics is a more promising method.

Today a large number of publications on the study of vapour mobile phases are available. But most of these publications report the use of water vapour. The vapours of organic solvents are used to a lesser extent, mostly for the acceleration of analysis and the production of linear adsorption isotherms. Systematic investigations of processes in chromatographic columns with organic vapour mobile phases (VMPs) have been given little attention. In this respect the work of Tsuda *et al.*¹ on the effect of vapour phases on sorbent modification is an exception to the rule. Therefore, systematic investigations of the modification of the polarity of stationary phases by vapour eluents have theoretical and practical interest. Based on this study, cheap and readily available sorbents can assume such characteristics which are inherent in the

rare liquid phases obtained by special synthesis. Another aspect of modification is that the sorbents assume polarities which are beyond the scope of the conventional Rohrschneider scale.

Hence, the object of our work is the study of variations of adsorbate-adsorbent interactions occurring during the modification process of the VMP liquid phase.

EXPERIMENTAL

Apiezon L, with a relative polarity, P , according to Rohrschneider of 8, and polyethylene glycol adipate (PEGA) ($P = 80$), *i.e.*, substances highly differing in polarities, were used as liquid phases. They were applied on Chromaton in an amount of 3% (w/w). Ethanol, acetone (polar) and hexane (non-polar) were used as eluting vapour agents. The feed of VMP into the column (300×0.3 cm) was effected by expulsion of solvent from a closed volume into the evaporator of a Tsvet-100 (U.S.S.R.) chromatograph equipped with a thermoconductivity detector. The flow-rate of VMP was maintained constant (4.2 cm/sec) for all the experiments and determined from the evolution period of a non-absorbing gas (helium). The choice of the column temperature was determined by two factors:

(1) The column temperature must slightly exceed the boiling point of the eluent; this results in maximal modification by the VMP

(2) The temperature must be identical during all analyses for convenience in comparing polarities of modified sorbents. The uniform temperature was taken as 90°C based on the properties of the VMP.

Substances of different classes, *i.e.*, *n*-alcohols, ketones, *n*-alkanes and aromatic hydrocarbons, were used for analyses.

RESULTS AND DISCUSSION

The concept of liquid phase polarity in chromatography is a relative one. The polarity of the same liquid phase, depending on the class of the compounds analyzed, can vary within broad limits. The scope of the "polarity" concept includes the energy of adsorbate-adsorbent interactions which varies significantly when passing from one adsorbate to another. Therefore it is more correct to talk about the polarity of any liquid phase with respect to the particular class of compounds analyzed. Accordingly, this work deals with the examination of the VMP effect on sorbent polarity for each of four classes of compounds analyzed separately.

Fig. 1 shows a plot of the relative polarities, P , of liquid phases modified by different VMPs *versus* the logarithm of the relative retention volume, V_{rel} , for 1-propanol, 1-butanol and 1-pentanol.

Compared to analysis using nitrogen, analysis of a mixture of alcohols in an ethanol current causes an increase in the retention times by a factor of 1.5-3, both in the column with Apiezon and in that with PEGA. The polarities, determined according to the Rohrschneider method, became 32.5 units for Apiezon and 88.5 units for PEGA instead of 8 and 80, respectively. This behaviour may be explained in terms of the balance between dispersion and orientation forces of interaction being shifted towards the orientation forces.

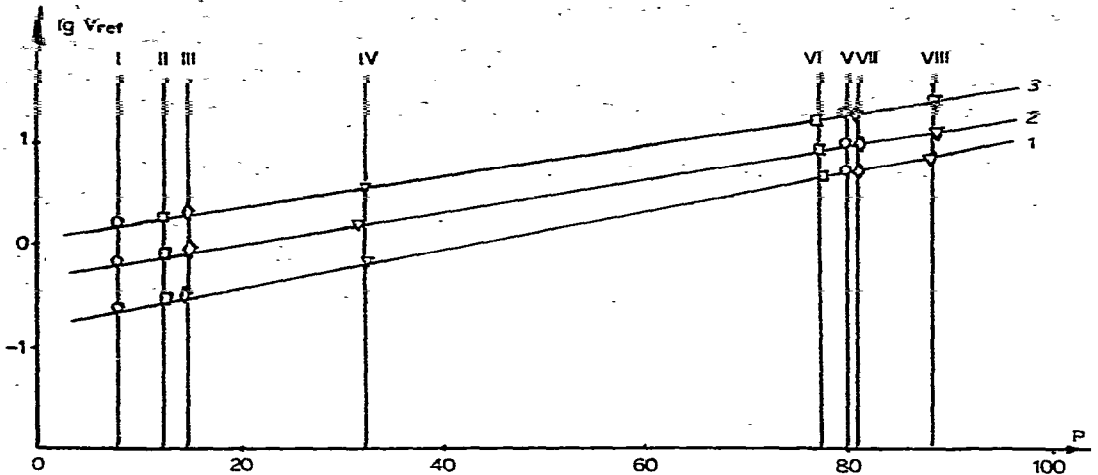


Fig. 1. Plot of $\log V_{ref}$ versus polarity of modified stationary liquid phases for 1-propanol (1), 1-butanol (2) and 1-pentanol (3). Apiezon L in vapours of the following compounds: I = nitrogen (O); II = hexane (□); III = acetone (◇); IV = ethanol (▽). PEGA in vapours of the following compounds: V = nitrogen (O); VI = hexane (□); VII = acetone (◇); VIII = ethanol (▽).

The modification of sorbents by acetone did not cause large alterations (polarity of Apiezon = 15, polarity of PEGA = 81) owing to its low boiling point and weak adsorption on the sorbent. Only its higher molecular weight, compared to nitrogen (58 vs. 28), increased the retention time of sorbates and the apparent polarity of the stationary liquid phases.

When hexane is used as eluent in the column with PEGA, the relation between dispersion and orientation is sharply changed in favour of dispersion forces, leading to a decrease in polarity. When *n*-alcohols interacted with non-polar Apiezon, the dispersion attractive forces were observed to be dominant. That is why the modifi-

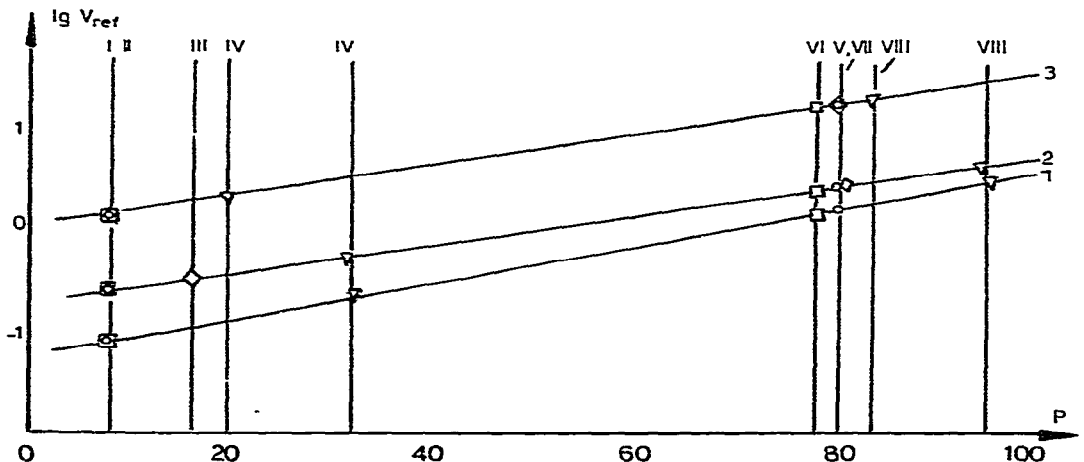


Fig. 2. Plot of $\log V_{ref}$ versus polarity of modified stationary liquid phases for acetone (1), methyl ethyl ketone (2) and acetylacetone (3). Key as in Fig. 1.

cation of Apiezon by non-polar hexane had no effect on the intermolecular interaction forces. However, the higher molecular weight of hexane reduces the diffusion into the mobile phase, the adsorbate molecules being retained in the stationary liquid. This leads to an increase in conventional chromatographic polarity (Apiezon polarity = 13 units).

Fig. 2 shows a plot of the polarities of liquid phases modified by different VMPs for acetone, methyl ethyl ketone and acetylacetone. As could be expected, while analyzing the polar ketones in vapours of polar ethanol, an increase in polarity of the stationary phases takes place. Thus, the increase in polarity for PEGA amounted to 94.5 and that for Apiezon to 32 Rohrschneider units. For acetylacetone, which is a diketone, the values of the relative variations of polarity amounted to 84 and 20 units on PEGA and Apiezon, respectively.

Modification of Apiezon by hexane vapours did affected neither its polarity nor the retention times of the components analyzed.

During the interaction of PEGA with ketones, the intermolecular interaction is due mainly to orientation forces occurring in the case of highly dipolar and small molecules². The use of hexane reduces the contribution of orientation forces to the total energy of the adsorbate-adsorbent interactions in the ketone-PEGA systems. A slight decrease in PEGA polarity is due to a change in the distribution coefficient between vapour and liquid phases.

Fig. 3 presents a plot of the polarities of liquid phases modified by different VMPs *versus* $\log V_{rel}$ for benzene, toluene and *p*-xylene. Aromatic hydrocarbons have specific structures that are revealed in the orientation and induction interactions. Therefore, regardless of the fact that benzene and *p*-xylene have a zero dipole moment (that of toluene amounted to 0.4 D), all the components are slightly polar. This conclusion is borne out by the typical (characteristic) slope of the dependence of $\log V_{rel}$ of sorbates *versus* conventional chromatographic polarity of the stationary phase.

Modification of sorbents by polar ethanol and acetone has the effect of increasing the significance of orientation and induction forces, these variations being very

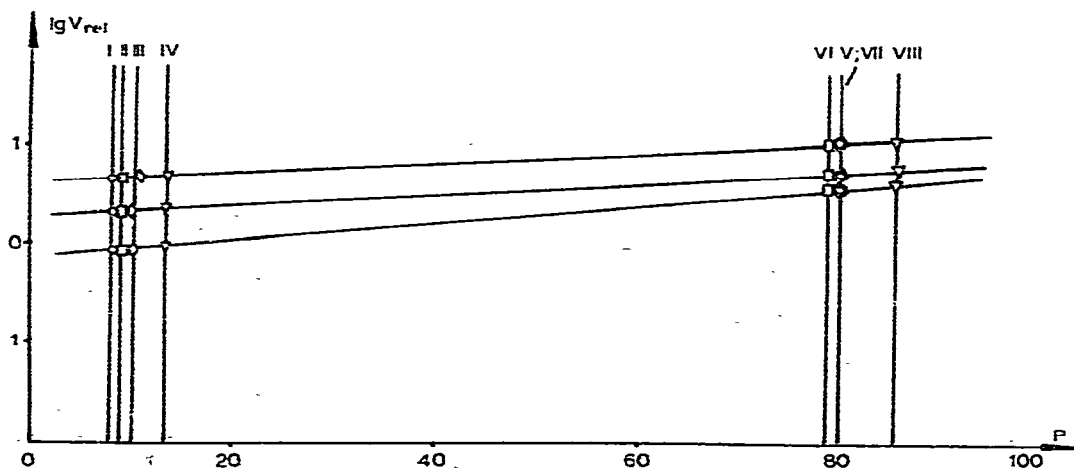


Fig. 3. Plot of $\log V_{rel}$ *versus* polarity of modified stationary liquid phases for benzene (1), toluene (2) and *p*-xylene (3). Key as in Fig. 1.

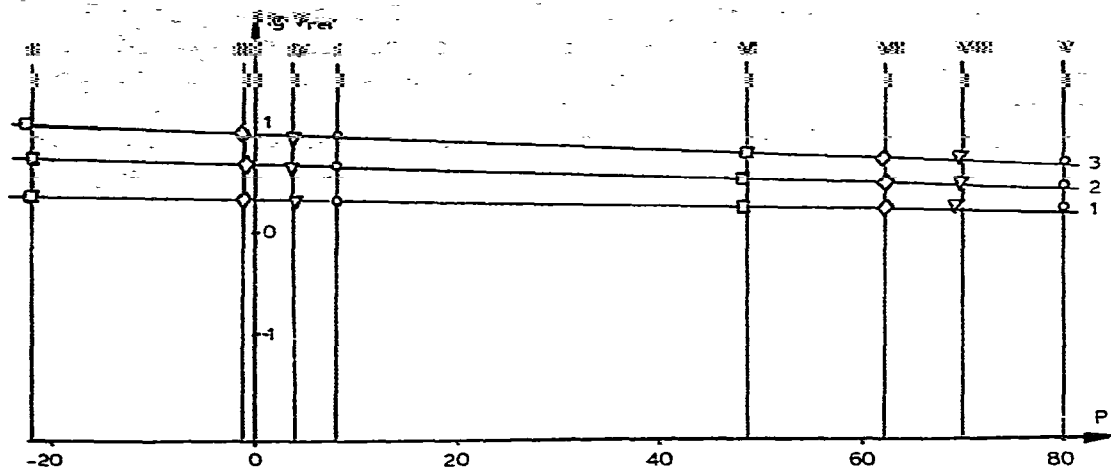


Fig. 4. Plot of $\log V_{rel}$ versus polarity of modified stationary liquid phases for octane (1), nonane (2) and decane (3). Key as in Fig. 1.

weak in acetone due to its volatility. As a result, while the PEGA polarity in an ethanol current amounted to 85, there were no variations in an acetone current. The polarity of Apiezon amounts to 14 in an ethanol current and to 10 Rohrschneider units in an acetone current.

Modification of sorbent by hexane had no effect as in the cases discussed previously.

Fig. 4 gives a plot of $\log V_{rel}$ versus the polarity of liquid phases modified by different VMPs for octane, nonane and decane.

Modification of Apiezon by hexane vapour causes an increase in the contribution of non-specific dispersion forces that must lead to a rise in retention time. The increase in molecular weight of the vapour phase leads to an increase in the retention time of the sorbate owing to a decrease in their diffusion into the mobile phase. This results in a decrease of polarity and an increase in elution time of the compounds analyzed.

It is interesting to note that the conventional polarity of Apiezon amounted to a negative value ($P = -22$), *i.e.*, the polarity of the modified phase is well below that of squalane which is generally accepted as the most non-polar phase with $P = 0$.

Modification of Apiezon by polar VMPs decreased the polarity to 4.0 in a current of ethanol vapour and to 1.0 in an acetone current.

The interaction of non-polar *n*-alkanes with the polar stationary phase of PEGA is determined mainly by dispersion forces, therefore its modification by both polar (acetone, ethanol) and non-polar (hexane) VMPs favours only an increase of dispersion forces. This modification decreased the polarity of PEGA in hexane vapour to 48.5, in acetone vapour to 62.5 and in a current of ethanol vapour to 70.0 Rohrschneider units.

On the basis of our work we have selected product pairs which are referred to as "invertants" because of the alteration of their elution order when passing from one mobile phase to another. An example of inversion is the reversal of the elution order of 1-pentanol and acetylacetone when passing from nitrogen vapour (where 1-penta-

nol was eluted first) to ethanol vapour (in which acetylacetone was eluted first).

The modification of stationary liquid phases by vaporized eluents is temporary and reversible. It allows their polarities to be varied directly and smoothly within a wide range.

Deliberate modification by vaporized mobile phases is an alternative for increasing the set of fixed liquid phases needed for conducting chromatographic studies.

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